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CORROSION AND CORROSION FATIGUE OF ALUMINUM ALLOYS: CHEMISTRY, MICROMECHANICS AND RELIABILITY (Reference: AFOSR Grant No. F49620-96-1-0245)

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SUMMARY

Lehigh University undertook a one-year multidisciplinary program of research, under AFOSR Grant No. F49620-96-1-0245 to continue to develop a basic mechanistic understanding of the material degradation processes of localized corrosion and corrosion fatigue crack nucleation and growth in aluminum alloys used in aircraft construction, and to formulate mechanistically based probability models for reliability assessments based on this understanding. This grant was an extension of the original 3-year program, under AFOSR Grant No. F49620-93-1-0426. This extension of research was initiated on 1 July 1996 and was extended to 31 December 1998. It is enhanced by a companion program sponsored by the Aging Airplanes Program of the Federal Aviation Administration (FAA) under Grant No. 92-G-0006. This final technical report summarizes research completed under Grant No. F49620-96-1-0245 over the period 1 July 1996 to 31 December 1998, and contains brief summaries of findings from Grant F49620-93-1-0426 and reflects contributions from the companion FAA sponsored program. Reprints and preprints of technical publications that resulted from these efforts are provided as a separate submission to the AFOSR Program Manager, and are available upon request to the Principal Investigator at Lehigh University.

1.0 Introduction

Performance, reliability, maintainability, and life cycle cost of aircraft and other aerospace systems depend to a large extent on those factors that affect the durability of airframe and propulsion system components. Durability is governed principally by material degradation through localized corrosion and corrosion fatigue crack nucleation and growth. Accordingly, to support the maintenance of existing aerospace structures (such as those of C/KC-135, C-141, C-5A, F-15, F-16 and T-38) and the development of Air Force structures of the 21st century, a methodology is needed for making stochastically tight estimates of structural life for conditions that are beyond the range of typical supporting data. Such a methodology would improve upon those employed currently in design, which are deterministically or statistically based and are only suitable for making interpolations within the bounds of existing data. The development of this methodology requires a quantitative understanding, characterization and modeling of the elemental processes of damage, and the integration of the various models into a suitable probabilistic framework for service life prediction.

This grant, under AFOSR Grant No. F49620-96-1-0245, represents the fourth year extension of a 3-year, multidisciplinary program of research awarded to Lehigh University as a part of the AFOSR University Research Initiation Program, under AFOSR Grant No. F49620-93-1-0426. The program was directed at the development of basic mechanistic understanding of the material degradation processes of localized corrosion and corrosion fatigue crack nucleation and growth in aluminum alloys used in aircraft construction, and the formulation of mechanistically based probability models for reliability assessments based on this understanding. Research under the original grant was initiated on 1 July 1993, with the experimental efforts focused on the 7000 series aluminum alloys. It is enhanced by an ongoing program on corrosion and fatigue of 2000 series aluminum alloys sponsored by the Aging Airplanes Program of the Federal Aviation Administration (FAA) under Grant No. 92-G-0006. Research under the current grant covers the period 1 July 1996 to 31 December 1997.

This final technical report summarizes research completed under the fourth year grant extension. For the sake of completeness, relevant information from Grant No. F49620-93-1-0426 and the FAA sponsored program are included.

2.0 Background and Objectives

The development of damage is illustrated schematically in Fig. 1, and is shown in a flow diagram in Fig. 2. The early stage is dominated by corrosion, in the form of pitting, and the later stage by corrosion fatigue crack growth. Within the context of these mechanisms, an upper bound of damage is to be defined in terms of structural reliability and damage tolerance considerations for mandating repairs. The planned research is focused, therefore, on the quantitative understanding and characterization, and kinetic modeling, of the following elemental processes:

Onset of localized corrosion damage (particularly, mechanisms and kinetics of pit nuclea-

tion and growth).

- Transition from pitting to fatigue crack growth.
- Early stages of corrosion fatigue crack growth (short-crack regime).
- Corrosion fatigue crack growth.

Formulation of a predictive model must include the probabilistic contributions from material properties and key variables on the rate of corrosion (particularly, pit nucleation and growth) and corrosion fatigue crack growth, and on the transition from corrosion to cracking.

The principal issues to be addressed are as follows:

- Identification and verification of key internal and external variables that control each of the aforementioned unit processes for corrosion and corrosion fatigue cracking and determination of the stochastic nature of each process.
- Quantification of the probability distribution function (including time variance) of each of the key variables.
- Development of a quantitative understanding of the rate controlling step and mechanism for each damage process, and formulation of a mechanistic (*deterministic*) model for each that describes the functional dependence on the key variables.
- Integration of mechanistic models and probability distribution functions, and formulation of mechanistically based probability models for life prediction and reliability assessment.

The objectives of the program are: (1) the development of basic understanding of the processes of localized corrosion and corrosion fatigue crack nucleation and growth in high strength aluminum alloys used in airframe construction, (2) the formulation of kinetic models for these elemental processes, and (3) the integration of these models into probabilistic models that can provide guidance in formulating methodologies for service life prediction and management.

3.0 Summary of Research

Efforts under the current programs included (i) further investigations of pitting corrosion and corrosion fatigue in the 2024-T3 and 7075-T651 (bare) alloys, principally at room temperature; (ii) extension of the mechanistically based probability approach for predicting (pitting) corrosion and corrosion fatigue life to reconcile the long-standing difference in the S-N (smooth specimen) and fracture mechanics approaches to fatigue; and (iii) provide a quantitative assessment of the probability for detection of damage by nondestructive inspection versus its probability of occurrence for service life management. Results in the various areas of research are briefly summarized, and publications and presentations of results developed under these AFOSR and FAA sponsored programs are listed in Section 4.0.

3.1 Pitting Corrosion

Studies of localized corrosion were focused upon pitting corrosion as a precursor to

corrosion fatigue cracking in the 2024-T3 and 7075-T651 (bare) alloys¹, and were carried out principally at room temperature in 0.5M NaCl solutions. (The chemical composition of these alloys are given in Table I.) The results showed that localized corrosion (pitting) resulted from galvanic coupling of the matrix with constituent particles in the alloys. Pitting was found to depend strongly on temperature and solution pH. The pitting rate increased with increasing temperature (corresponding to an activation energy of about 40 kJ/mol), and was higher at more basic pH levels. The process is very complex and involved 3-D interactions with the constituent particles. Corrosion sensitivity depends on the orientation, being more severe in the thickness orientation (the orientation that is more representative of the surface of a rivet or fastener hole) because of local segregation of the constituent particles.

To better understand particle-induced localized (pitting) corrosion, detailed studies were carried out on the transverse sections of these alloys at room temperature, by *in situ* monitoring and by post-corrosion examinations using optical and scanning electron microscopy. A replication technique was developed to facilitate examinations of the morphology of corrosion pits in three dimensions, and measurements of pitting kinetics. Identification of the constituent particles and observations of particle-induced galvanic corrosion were carried out by transmission electron microscopy (TEM), along with measurements of galvanic current between pure aluminum and model compounds that are representative of the composition of certain constituent particles. Results from these studies are briefly summarized.

Constituent Particles -- Two types of constituent particles were identified by energy dispersive x-ray spectroscopy (EDS) in the scanning electron microscope (SEM): those particles that are anodic and those that are cathodic with respect to the matrix. In the 2024-T3 alloy, the anodic particles typically contained Al, Cu and Mg, whilst the cathodic ones contained Al, Cu, Fe and Mn. Anodic and cathodic particles in the 7075-T651 alloy, on the other hand, contained Al, Cu, Mg and Zn, and Al, Cu, Fe, Cr, Mn and Zn, respectively. The density of these particles (with projected surface area greater than 1 µm²) was about 3,000 particles/mm² in the older 2024-T3 alloy, versus about 1,500 particles/mm² in the newer 7075-T651 alloy. The distributions in particle sizes for the two alloys are similar. Elemental maps showed that nearly 75% of the constituent particles in the 2024-T3 alloy are anodic, whereas over 80% of the particles in the 7075-T651 alloy are cathodic. Analytical electron microscopy (AEM) and X-ray microprobe analyses showed that the anodic particles in the 2024-T3 alloy are principally Al₂Cu and Al₂CuMg. The cathodic particles, on the other hand, are identified with complex intermetallics of the type (Fe,Mn)_xSi(CuAl)_y, and appear to be modified forms of Al₈Fe₂Si or Al₁₀Mn₃Si. In the 7075-T651 alloy, the cathodic particles are identified as orthorhombic Al₂₃Cu Fe₄ that contain small amounts of Cr, Mn and Zn. The remaining particles in the AEM samples of this alloy are principally amorphous SiO₂, which are inert. The corrosion potential of some of the intermetallics compounds, metals and alloys are given in Table II.

<u>Pitting Corrosion</u> -- Pitting in these alloys, in 0.5M NaCl solutions, showed that localized pitting corrosion was associated with *constituent particles*. A distinction was drawn between

 $^{^{1}}$ The 2024-T3 alloy sheet was of 1960s vintage, and the 7075-T6 alloy sheet was of 1980s vintage.

anodic and cathodic particles; with anodic particles tending to dissolve themselves, while cathodic particles promoting dissolution of the adjacent matrix. Two modes of pitting corrosion were identified: namely, (i) general pitting over the specimen surface, and (ii) severe localized pitting at selected sites. General pitting occurred almost immediately upon specimen immersion, and led to the formation of small, shallow pits over the entire specimen surface. Each pit was clearly identified with a constituent particle on the specimen surface, with particle or matrix dissolution determined by the nature (anodic or cathodic) of the particle. Severe localized pitting at selected sites was attributed to the interactions of the matrix with a cluster or clusters of constituent particles. The particle clusters formed local galvanic cells to sustain continued matrix dissolution, and resulted in the larger and deeper pits.

Figure 3 shows scanning electron micrographs (SEM micrographs) of the cross section of pits formed from such clusters of constituent particles, along with an inset of the pits at the specimen surface. The larger of the two pits is approximately 500 µm long and 70 µm wide at the surface, and approximately 300 µm deep at this section; the overall shape reflects the planar distribution of constituent particles in this alloy. This type of severe localized pits has been identified as nuclei for corrosion fatigue cracking. The 3-dimensional nature of the severe pits is captured by the comparison of the corroded LS (longitudinal-thickness) surface of a 1.6-mm-thick 2024-T3 aluminum alloy sheet, after 500 h exposure to 0.5M NaCl solution, with the corresponding epoxy replica in Fig. 4. The 3-dimensional nature of these pits is best seen through the use of stereo imaging techniques (not shown here). The severe pits tend to be concentrated (>50%) along the mid-thickness region of the sheet, and are narrow and long, and substantially larger than the surface opening. For example, the surface length and width of pit 4 are 230 and 80 µm, respectively, as compared to an overall length and width of over 430 by 130 µm shown by the replica. The height (depth of penetration) of the pits ranged from about 100 to over 300 µm. The replicas show substantial corrosion attack beneath the specimen surface, and potential link up of several pits into a single large pit of a complex shape (see, for example, pits 5, 6 and 7). They show that surface measurements alone would underestimate (indeed, provide incorrect estimates of) the extent and kinetics of pitting attack.

High magnification SEM micrographs of the replica of pit 2, in plan and side views, in Fig. 5 show the typically complex form of a severe corrosion pit. The shape of the replica might be likened to that of one-half of a pecan or walnut, with the center representing the small pit opening at the surface and the rest of the cavernous pit below the surface. Its appearance is consistent with the postulated role of constituent particles in promoting pitting corrosion. The individual rounded features are attributed to galvanic corrosion of the matrix by the cathodic-behaving constituent particles in the alloy, and the overall planar appearance, to the planar array of these particles in the rolled sheet. The open space seen in Fig. 5b suggests the role corrosion played around a particle (or a cluster of particles) at the surface in allowing the electrolyte to penetrate into the alloy and effect substantial corrosion beneath the surface.

<u>TEM Studies of Particle-Matrix Interactions</u> -- To provide unambiguous confirmation for the role of constituent particles in promoting pitting, a series of experiments were carried out with the aid of transmission electron microscopy (TEM) on the 2024-T3 and 7075-T651 aluminum

alloys. The constituent particles were first identified and the TEM (thin foil) samples were then repeatedly immersed in 0.5M NaCl solution and re-examined for galvanic corrosion attack. Figure 6 shows a pair of TEM micrographs to illustrate the typical galvanic corrosion of the matrix that results from the coupling with a cathodic constituent particle in the 7075-T651 alloy. The larger semi-circular region in Fig. 6a represents oxides that had been left behind by the corrosion. The smaller semi-circular depression represents the original position of the particle in the thin foil; the particle having fallen out during corrosion. The relative positions of the particle and the corroded region are shown in Fig. 6b, with the particle photographically superimposed back into its original position. The size of the corroded region (at about 5X the particle size) a*p-1Xttests to the "throwing power" of the particle.

Similar results were obtained on the 2024-T3 alloy, with dissolution of the alloy matrix around each of the particles or clusters of particles. The Al₂CuMg particles in this alloy are anodic with respect to the matrix; Al₂Cu, however, is cathodic relative to pure aluminum and is thought to be anodic to the alloy. The (Fe,Mn) containing particles are cathodic to the alloy matrix. In essence, all of the particles appeared to behave cathodically in promoting matrix dissolution irrespective of their expected anodic or cathodic character. The extensive matrix dissolution observed around the nominally anodic Al₂Cu particles is attributed to the plating of Cu back onto the particles during corrosion. Even though the Al₂CuMg particles dissolved rapidly, some matrix dissolution was noted as a result of Cu deposition, or Cu enrichment through preferential dissolution of Al and Mg from these particles.

Dissolution current densities were estimated based on the estimated amounts of material removed by galvanic corrosion and reflected *anodic* or *cathodic* control by the particles. For the *anodic* (Al₂CuMg) particles, the estimated current density was about 180 μ A/cm² at room temperature. The estimated values were about 200 μ A/cm² and 40 μ A/cm², respectively, for Al₂Cu and the (Fe,Mn) containing particles.

Electrochemical Measurements on Model Compounds -- To better understand particle induced corrosion, the galvanic coupling between model compounds Al₃Fe and 70Al-22Fe-6Cu-2Mn (alloys A and B) and high-purity aluminum was investigated. The galvanic current between the model compounds and pure aluminum in 0.5M NaCl (pH≈7) and 0.5M NaCl+0.07M AlCl₃ (pH≈3.5) solutions (exposed to air) at room temperature were measure as a function of the ratio of surface areas of the electrodes. The results are shown in Figs 7 to 10. They show that the galvanic current density varied with the ratio of surface areas of the model compounds (*cathode*) and Al (*anode*). When the cathodic area is small, current flow is limited by rate of reactions at the cathodic surface and is reflected by a constant cathodic current density. When the cathodic surface is large relative to the anodic surface, on the other hand, current limitation is transferred to the anode (or Al) and the process proceeded at a constant anodic current density.

For the Alloy A-Al couple in the neutral 0.5M NaCl solution, the limiting cathodic and anodic current densities were found to be about 38 and 31 μ A/cm², respectively. For the Alloy B-Al couple, they are 46 and 32 μ A/cm², respectively. These limiting cathodic current densities are consistent with those estimated for the cathodic particles in the 2024-T3 and 7075-T651

alloys. The limiting cathodic current densities in the acidic solution, on the other hand, are nearly five times higher, at 140 and 147 μ A/cm² for the Alloy A-Al and Alloy B-Al couples, respectively. The limiting anodic current densities are lower, at 22 and 26 μ A/cm² for the same couples, respectively. The higher cathodic current densities in the acidic solution is consistent with the expected increase in the rate of pit growth that result from acidification of the environment within a corrosion pit. Estimates of pitting around individual constituent particles (*i.e.*, general pitting) were made. The pit growth rates were found to be consistent with the postulated cathodic control by the constituent particles and the measured current densities.

Mechanistic Models and Model Clusters -- The fact that dissolution can take place around all or most of the constituent particles provides an important bridge for the development of the larger severe pits. These findings confirm the original postulate for particle induced pitting in these aluminum alloys. Based on these, and the previous SEM observations, a conceptual model for corrosion induced by a single particle is proposed, Fig. 11. A conceptual model for pit growth associated with a cluster of particles is depicted in Fig. 12. The multi-particle interactions within a pit (or occluded region surrounding the pit), however, make the problem much more challenging. Because this severe localized pitting is clearly linked to corrosion fatigue crack nucleation, emphasis has been placed on the development of mechanistic understanding and modeling of this process. This effort will be continued under the follow-on program of research. The quantitative, mechanistic model will need to incorporate potential distribution around the particle, and will be integrated into a model for severe pitting that involves clusters of constituent particles.

Because of the complex 3-dimensional shape of severe corrosion pits and the random location and distribution of particle clusters in commercial alloy, it is nearly impossible to obtain reliable measurements of the kinetics of pit growth. With the successful use of model compounds in the aforementioned electrochemical studies, the feasibility of using these compounds to produce *controlled* particle clusters of specified form, density and particle size was demonstrated. Powders of selected elements or compounds were mixed with pure aluminum power to produce mixtures with specified volume fractions. Each mixture was packed into the drilled out center of a pure aluminum rod. The rod was then extruded to sinter the powders and produce a cylindrical zone of particle cluster of uniform average density.² Sections of the rod then can be used serially for characterizing the kinetics of pit growth. Figure 13 shows the cross-section of such a rod with Cu particles, and Fig.14 shows a similar section which had been exposed to 0.5M NaCl solution for 70 h at 343 K. These results provide *proof of concept*, and more comprehensive experiments are planned for the continuation of research.

3.2 Transition from Pitting to Fatigue Crack Growth

Studies of the 2024-T3 and 7075-T651 alloys showed that fatigue failure, by-and-large, resulted from a *single* nucleation site. Hence, a dominant flaw model for corrosion and corrosion fatigue would appear appropriate. The pit-to-crack transition size (or crack nucleation size),

² Dr. Vivek Sample, Alcoa Technical Center, Tech Center, PA

however, was found to depend on the cyclic-load frequency; being larger at lower frequencies. This frequency dependence reflected *competition* between pitting corrosion and fatigue. Corrosion fatigue crack nucleation, therefore, must be understood in terms of the competition between pitting and fatigue crack growth, and is characterized by the transition to fatigue crack growth from a growing pit. Two criteria for this transition were proposed and validated. They are: (i) the cyclic stress intensity range (ΔK) for an equivalent crack must exceed the fatigue crack growth threshold ΔK_{th} , and (ii) the time-based fatigue crack growth rate must exceed the pit growth rate; i.e.,

$$\Delta K \ge \Delta K_{th}$$
 and $\left(\frac{dc}{dt}\right)_{crack} \ge \left(\frac{dc}{dt}\right)_{pit}$

The use of 'c' in the growth rate criterion gives recognition to the fact that the aspect ratios of most of the pits (or equivalent cracks) would lead to a higher ΔK at the surface.

A corrosion/fatigue map is proposed to provide a graphical view of these criteria. It delineates the transition ΔK (ΔK_{tr}) in relation to the cyclic load frequency f, with the applied cyclic stress range as a parameter. The map is constructed by assuming a constant volumetric rate law for pit growth and a power-law for fatigue crack growth, with an exponent n, and is shown schematically in Fig. 15. The transition ΔK_{tr} is given by one of the following relationships, which divides the ΔK versus 1/f space into two regions in which either fatigue crack growth or pit growth predominates:

$$\Delta K_{tr} = \Delta K_{th}$$

$$\Delta K_{tr} = \left[\frac{(1.12k_t \Delta \sigma) t^4}{2} \frac{C_p}{C_F} \frac{\beta_{tr}^2}{\Phi_{tr}^4} \right]^{\frac{1}{n+4}} \left(\frac{1}{f} \right)^{\frac{1}{n+4}}$$

where, k_t is the stress concentration factor of the hole; $\Delta \sigma$ is the applied cyclic stress range; C_P and C_F are the pit and fatigue crack growth rate coefficients, respectively; and β_{tr} and Φ_{tr} are the aspect ratio and shape factor (elliptical integral) for the equivalent semi-elliptical crack at transition. The first of these relationships simply reflects exceedance of the fatigue crack growth threshold (ΔK_{th}). The second, on the other hand, reflects a higher value of ΔK_{tr} required by rate competition. Data on pit-to-crack growth transition for the 2024-T3 alloy are shown in Fig. 16 to illustrate the efficacy of this representation.

Nucleation of fatigue crack growth from pre-corroded (*i.e.*, pre-pitted) specimens provides additional insight for the transition criteria. A series of experiments was performed by Harmsworth³ to study the influence of pre-corrosion on the lives of a 2024-T4 aluminum alloy in

³ Clayton L. Harmsworth, "Effect of Corrosion on the Fatigue Behavior of 2024-T4 Aluminum Alloy", ASD TR 61-121, Aeronautical Systems Division, Wright-Patterson AFB, Ohio, July 1961.

rotating bending fatigue. The reported data include the pre-corrosion times, pit depths and subsequent fatigue lives at a constant stress amplitude $\Delta\sigma$ of 179 MPa. The experimentally observed fatigue lives correlated well with the crack growth lives predicted on the basis of the initial pit depths and appropriate growth law. The inference from this correlation is that fatigue cracks appear to grow immediately once the nucleation criteria are satisfied, which provides support for the proposed transition (nucleation) criteria. Nucleation time, if present at all, may be reasonably neglected. This information is used to reconcile the long-standing difference in the S-N and fracture mechanics approaches to fatigue. The finding is summarized in Section 3.4.

3.3 Short-Crack Growth

Studies of the transition from pitting to corrosion fatigue crack growth (or crack nucleation) suggested that the pit size at transition is in the range of 40 to 200 μ m (or 0.04 to 0.2 mm). The extent of fatigue crack growth of interest (for example, in fuselage lap joints), on the other hand, is on the order of a few millimeters. As such, characterization and modeling of the early stage (or chemically short regime) of corrosion fatigue crack growth is important to the accurate and reliable assessment of service lives of aircraft structures.

Experiments were performed to study the fatigue crack growth response of 2024-T3 and 7075-T651 (bare) alloy sheets in 0.5M NaCl solutions at room temperature, using single-edge-cracked tension (SEC(T)) specimens tested under constant stress intensity range (ΔK) conditions at 10 Hz. The relationship between crack growth rate and crack length (0.5 to 15 mm) was determined at ΔK of 4, 5, 6, 7, 8 and 10 MPa \sqrt{m} , with R = 0.1. Three dissolved oxygen levels ([O₂] = 0, 7 and 30 ppm) were investigated. Experiments in high-purity oxygen and water vapor were also conducted to provide for comparison.

The results for the two alloys are summarized in Figs 17 and 18. They show no crack length dependence (i.e., no short-crack effect) in the deaerated solution ($[O_2] = 0$ ppm). There was also no crack length dependence in high-purity oxygen and water vapor (not shown). The crack growth rates, however, showed a strong influence of environment and were nearly 10 times faster than those in high-purity oxygen. Chemically short-crack growth behavior was observed in some of the aqueous environments. The behavior is quite complex and depends on ΔK and dissolved oxygen concentration (see Figs 17 and 18). The effect manifested itself in increased crack growth rates at a crack length of 0.5 mm and subsequent decrease to the long-crack rates at longer crack lengths. The increase in rate was as much as a factor of two over the long-crack rate at the lower ΔK levels (see, for example, data for $\Delta K = 5$ MPa \sqrt{m}). The crack length at transition to long-crack growth depended on ΔK . The short-crack effect also gradually disappeared at higher ΔK levels; the particular level depended on oxygen concentration and the alloy.

Fractographic examinations showed no noticeable differences in the micromechanisms for crack growth between water vapor and aqueous solutions. Some difference was noted, however, between the short and long cracks, particularly for the 7075-T651 alloy. These observations are consistent with a single cracking (hydrogen embrittlement) mechanism, and showed that the effect resided with the external chemical environment. Its absence in the

deaerated solution strongly indicates that the effect is associated with dissolved oxygen near the crack tip, which altered the kinetics of electrochemical reactions and the subsequent embrittlement. A model for estimating the dissolved oxygen concentration at the crack tip was developed, based on consideration diffusive and convective transport of oxygen and other species, as well as oxygen reduction along the crack surfaces. The predicted reduction in oxygen concentration correlated reasonably well with the observed effect of crack length. The model, however, was not able to account for the disappearance of short-crack effect with increasing ΔK .

Because much of the corrosion fatigue life is expected to be in the short-crack regime (i.e., from a nucleating corrosion pit to several millimeters), the crack growth response can significantly influence the service lives of aircraft structures. This task, therefore, is being continued on the 7075-T651 alloy.

3.4 A Crack Growth Perspective on S-N Curves

Recognizing the important roles of micro-constituent particles and particle-induced severe corrosion pits in fatigue crack initiation, an attempt was made to reconcile the long-standing (apparent) differences between the underlying approaches in fatigue, and in response. In a recent reexamination of a study by Harmsworth on the effect of pre-corrosion on fatigue in a 2024-T4 aluminum alloy, it was found that the observed fatigue lives could be correlated with the crack growth lives from the measured initial pit sizes (see Section 3.2). In other words, crack nucleation time, if present at all, could be reasonably neglected. One might, therefore, begin with a postulate that the observed fatigue life is governed by the size of the initiating damage (particle or pit) and the rate of subsequent crack growth. For simplicity, fatigue crack growth was assumed to follow a power-law of the following form:

$$\frac{da}{dN} = C_F (\Delta K - \Delta K_{th})^n; \qquad \Delta K = \beta \Delta \sigma \sqrt{a}$$

where C_F is crack growth rate coefficient; ΔK_{th} is the fatigue threshold ΔK ; β is a geometric parameter; and n is the power-law exponent. The material parameters C_F and ΔK_{th} are both functions of the test environment, as well as temperature and other factors. For these estimates, the initiating constituent particle, or severe corrosion pit, is assumed to be hemispherical in shape and to be equivalent to a semi-circular crack with the same radius (with $\beta = 2.2/\pi^{1/2}$). Because the initiating particle and pit sizes are very small, the final crack size at fracture could be neglected, and the predicted fatigue (crack growth) life is given, from integration of the rate equation, simply by:

$$N_F \approx \frac{2}{(n-2)C_F \beta^2 \Delta \sigma^2 (\Delta K_i - \Delta K_{th})^{(n-2)}} \left[1 + \frac{(n-2)\Delta K_{th}}{(n-1)(\Delta K_i - \Delta K_{th})} \right]$$

where ΔK_i correspond to the radius a_0 of the initial pit. Fatigue lives at different stress levels (from 100 to 400 MPa) were calculated, for an initial pit radius of 10 to 200 μ m, using n = 3.55

(estimated from data on the 2024-T3 alloy), and the following parameters: $C_F = 1.3 \times 10^{-11}$ (m/cyc)(MPa \sqrt{m})^{-3.5} and $\Delta K_{th} = 0.95$ MPa \sqrt{m} for air; and $C_F = 3.95 \times 10^{-11}$ (m/cyc)(MPa \sqrt{m})^{-3.5} and $\Delta K_{th} = 0.5$ MPa \sqrt{m} for the 0.5M NaCl solution. The estimated fatigue lives are shown in Fig. 19. For the estimated life in air, a particle radius of 10 μ m was used. The choice of ΔK_{th} is somewhat arbitrary, and reflected a recognition that their levels associated with a corrosion pit may be substantially lower than that observed from long-crack experiments.

The estimated results correlated well with the conventional S-N data for corrosion fatigue; with a reduction in life and a lowering of the endurance limit. The 'smooth specimen' fatigue life is clearly identified with crack-growth life from an initiating stress concentrator (a constituent particle or a corrosion pit), and the endurance limit, with the ΔK_{th} associated with it. The reductions in fatigue lives are associated with increases in the size of a corrosion pit. The response may be interpreted simply in terms of the effect of pre-corrosion (or pre-pitting). It may be viewed also as a reflection of fatigue at different loading frequencies; with the lower frequencies producing larger pits and shorter fatigue lives. The interpretations are consistent with the set of transition criteria derived from the aforementioned studies (see Section 3.2), and provide a framework for further reconciliation between the conventional and fracture mechanics (or initiation versus growth) approaches to corrosion fatigue.

3.5 A Mechanistically Based Probability Approach to Life Prediction

A dominant flaw, probability model for pitting and corrosion fatigue has developed. This model assumes pitting corrosion proceeded at a constant volumetric rate. Transition from pit (hemispherical) to crack (semi-circular) is based on a matching of the stress intensity factor for an equivalent semi-circular crack against the fatigue crack growth threshold. A power-law model is used to represent subsequent fatigue crack growth. The models for the elemental processes are assumed to capture some of the key mechanistic features, and provide reasonable predictions of response. The overall model incorporates initial defect (or particle/cluster) size, corrosion rate, fatigue crack growth rate coefficient, and fatigue crack growth threshold (ΔK_{th}) as random variables, and permits examinations of the contribution of each of these variable to the distribution in life.

This simplified mechanistically based probability model was used in estimating the probability of occurrence (POO) of damage in aircraft components and structures subjected to corrosive environments, and in considering the difference between damage accumulation and its detection by nondestructive inspection (NDI). Specifically, the approach has been used to illustrate the relationship between the POO and probability of detection (POD) of flaw sizes. The model for the damage growth incorporates simplified models from first principles of pitting corrosion and corrosion fatigue crack growth. Similarly, the baseline distribution for the POD of damage is expected to depend on structural configurations and NDI techniques, but it is not yet well established. The distribution used herein reflects the 1990 state-of-the-art for NDI based on eddy current systems. It is recognized that both the modeling and damage detection methodologies can be improved substantially.

This assessment is at the heart of airworthiness assurance. A component or structure is airworthy, if its integrity can be assured beyond its current state throughout the projected period of operation until the next scheduled inspection. Thus, airworthiness assurance depends critically on the quality of the current state and on the accuracy of that assessment. The significance of material damage on residual strength or life is not understood well; however, any suitable analysis must estimate the damage accumulation under the projected service environment given the current state of damage. Furthermore, this information should be an integral part of NDI/NDE and maintenance scheduling to assess the effectiveness of the POD and the need for repairs.

For the purpose of illustration, plot of the POO that the flaw size exceeds a specified level a at a given time t is shown in Fig. 20 in Weibull probability form. The times, ranging from 500 to 4500 days, encompass the typical behavior. For the shorter times, 500 to 2500 days, pitting predominates; however, for the longer times cracking is critical. This is depicted by the rather abrupt change in the shape of the probability curves. There is variability in the transition size a_{tr} from pitting to cracking due to the underlying rvs, but it ranges between 0.6 and 0.9 mm. Clearly, the probability of finding a large flaw for longer times, and greater damage, is quite high. The POD baseline for NDI based on eddy current systems 4 is also shown in Fig. 20. It has the following form:

$$\Pr\{\text{detecting a flaw} > a\} = \left\{1 + \exp\left[-\frac{\pi}{\sqrt{3}} \left(\frac{\ln(a - a_{\min}) - \ln(m)}{s}\right)\right]\right\}^{-1}$$

where m is the median detectable flaw size, s is a scaling parameter related to the variability in detection, and a_{\min} is the minimum detection level. The parameters for the POD baseline are assumed to be m = 1.27 mm, which is based on the current damage tolerance approach, s = 0.572 $\ln(mm)$, and $a_{\min} = 0$. Thus, $\Pr\{\text{detecting a flaw} > 2.54 \text{ mm}\} = 0.90$.

This POD baseline is used commonly as a reference. The portion of the figure of concern is that above the POD baseline in which the actual POO of a flaw exceeding a is greater than the POD. If the flaw size is small, the concern is not structurally significant. If the flaw size is larger, however, the consequence is amplified. For example, for $t = 4500 \, days$, the POO of a flaw size greater than 1.27 mm is about 50%, but the POD for that flaw size is only 50%. In other words, about half of those flaws would go undetected. For even larger flaw sizes, the POD appears to be adequate, but their impact on flight safety may no longer be acceptable. Nevertheless, a caution must be given. As indicated in Fig. 20, the POO of a very large flaw is small, which means that to certify that such a flaw does not exist would require a thorough search over an extensive area.

The tension between the POO and the POD is highlighted in Fig. 21, which shows the average flaw size versus time for applied stresses of 100, 200, and 300 MPa. Pitting is dominant up to t_{tr} , after which cracking controls the flaw growth. For $\Delta \sigma = 200$ and 300 MPa there is a

⁴ A.P. Berens et al., "Risk Analysis of Aging Aircraft Fleets: Volume 1-Analysis," USAF WL-TR-91-3066 (1991).

sharp transition from pitting to cracking, but for $\Delta \sigma = 100$ MPa the transition is gradual. The three dashed horizontal lines represent the USAF allowable size for a single flaw (1.27 mm), the NDI POD of 90% (2.54 mm), and a reasonable allowable limit for a panel (10.0 mm). All of these values are in the cracking domain regardless of the magnitude of the applied stress. The more striking observation is that the remaining life after the flaw exceeds the allowable size of 1.27 mm (where the POD is only 50%) is quite small. For $\Delta \sigma = 200$ and 300 MPa, the remaining average life is only 10 and 5% of the total, respectively. The situation is not as severe for $\Delta \sigma = 100$ MPa, with the remaining average life approximately 30% of the total; but the fraction diminishes to just 15% beyond the 90% POD value.

A comparison showing the effect of localized corrosion for $\Delta \sigma = 300$ MPa is given in Fig. 22. The predicted average damage response for two models, one incorporating pitting corrosion and the other without, for identical initial flaw size are presented. The model, including pitting corrosion predicts a significantly shorter life than the model that is based purely on CFCG. An alternative procedure is to compare the crack growth lives starting with and initial flaw size of a_{th} (no pitting corrosion) versus one equal to a_{tr} (with pitting). Here, pitting corrosion is found to reduce the fatigue life by almost 4 orders of magnitude, which is extreme, but is consistent with the results in Fig. 16. Furthermore, after the alloy is exposed to the deleterious environment, the time for pitting corrosion to progress to a size of a_{th} is only on the order of a few days. Thus, pitting can have a rather severe impact on the life and integrity of a structure. Clearly, more stringent requirements for setting allowable design limits are needed.

Equally important is the ability to detect the damage precisely. For NDI/NDE, the estimates shown in Fig. 22 pose an acute dilemma. Typically inspection intervals are established as a fraction of the predicted life of a structure. For this example, however, a safe inspection criterion based on an assumption of pitting and CFCG together would be only about 10% of the life predicted by considering only CFCG. In other words, inspection would be necessary relatively soon after the unprotected alloy has been exposed to the environment. In reality, aircraft structures are protected quite well; however, when they have been compromised by corrosion, corrective action becomes urgent. The consequence of this observation is that the resolution for NDI must improve drastically. The POD needs to be high, at least 90%, for flaw sizes between 10 and 50 times smaller than that indicated by the baseline POD shown on Fig. 20. Current NDI/NDE methods do not provide suitable accuracy. Coupled to this need for detecting rather small damages is the mandate for inspecting extremely large structures, some of which have nearly inaccessible locations. Obviously, the relationship between allowable limits, actual damage sizes, and detection accuracy is critical for proper aircraft maintenance and management. Coordinated studies in this area are recommended.

It is recognized that the foregoing example does not model a real structure, but the implications for the probability of detection by NDI/NDE are clear. This model has been modified to account for corrosion and fatigue from an open circular hole, with the inclusion of a further transition from the semi-circular crack at an open-hole to a through-thickness crack. Further analyses using this modified model are being conducted under the follow-on program.

3.6 Interactions with Wright Laboratory

To facilitate the reduction of mechanistic understanding developed under these programs to practice, a new task was added in 1994 with funding from the Flight Dynamics Directorate at the Air Force Wright Laboratory. The objective of this task was to define work that would be needed to incorporate mechanistic models into the current Air Force structural integrity and durability analysis methodologies, with specific emphasis on MODGRO (now designated as AFGROW) and PROF. The feasibility for incorporating a mechanistically based probability approach into the PC-based fatigue life analysis program MODGRO, to include key *internal* and *external* variables (in addition to initial crack size), was demonstrated. This study showed that the influences of temperature, material properties, the coupling of fatigue loading and thermal profiles, and load sequencing on fatigue lives under spectrum loading could be incorporated into a mechanistically based probability framework.

The efficacy of this approach has been demonstrated and is illustrated in Fig. 23. These results show the influence of temperature and the combined effects of variations in load and temperature on the CDFS (cumulative distribution functions) for fatigue lives under variable amplitude loading, using the random load spectra FALSTAFF. These results indicate that temperature can significantly affect fatigue life. The influences of temperature are manifested directly through its effect on crack growth rates, and indirectly through its effect on yield strength and its role in crack growth retardation (*i.e.*, load-interaction effects). The results and a modified computational program have been forwarded to Mr. James Harter at AFWL/FI for potential incorporation into AFGROW.

These results demonstrate the viability and potential value of the mechanistically based probability approach for service life prediction, and indicate that understanding developed under these and similar basic research programs can be readily transferred to ongoing Air Force support activities. Further research is needed to develop improved mechanistic models for fatigue crack growth (in both the short- and long-crack regimes), and to incorporate a mechanistically based model for pitting into the fatigue analysis programs.

4.0 Presentations and Publications

Presentations and publications based on results from this program and the FAA sponsored program are given in the following subsections.

4.1 Presentations

"A Probabilistic Approach to Life Prediction for Corrosion Fatigue Crack Growth", **Robert P. Wei**, Boeing Commercial Airplane Group Seminar, Seattle, WA, October 17, 1991.

"A Mechanistically Based Probability Approach to Life Prediction for Corrosion and Corrosion Fatigue of Airframe Materials", **R. P. Wei**, FAA/NASA Workshop on Corrosion, ALCOA, PA, November 22, 1991.

- "A Mechanistically Based Probability Approach to Life Prediction for Corrosion and Corrosion Fatigue of Airframe Materials", **Robert P. Wei** and D. Gary Harlow, International Workshop on Structural Integrity of Aging Airplanes, Atlanta, GA, April 1, 1992.
- "A Mechanistically Based Probability Approach to Life Prediction for Corrosion and Corrosion Fatigue of Airframe Materials", **Robert P. Wei** and D. Gary Harlow, Seminar at Exxon, NJ, August 4, 1992.
- "Mechanistic Understanding of Corrosion and Corrosion Fatigue and Prediction of Service Life", R. P. Wei, ALCOA Seminar, Alcoa Center, PA, December 7, 1992.
- "Corrosion and Corrosion Fatigue of Airframe Materials", R. P. Wei, NASA Research Center, VA, April 27, 1993.
- "Corrosion and Fatigue of Aluminum Alloys: Chemistry, Micromechanics and Reliability", R. P. Wei and **D. Gary Harlow**, Workshop on Aging Aircraft Research, Georgia Institute of Technology, Atlanta, GA, April 27, 1993.
- "A Probability Model for Predicting Corrosion and Corrosion Fatigue Life of Aluminum Alloys", **D. Gary Harlow** and R. P. Wei, NIST and Temple University Conference, Gaithersburg, MD, May 4, 1993.
- "A Mechanistically Based Probability Approach for Predicting Corrosion and Corrosion Fatigue Life", **R. P. Wei** and D. Gary Harlow, 17th Symposium of the International Committee on Aeronautical Fatigue", Stockholm, Sweden, June 9, 1993.
- "A Dominant Flaw Probability Model for Corrosion and Corrosion Fatigue", D. Gary Harlow and **Robert P. Wei**, 12th International Corrosion Congress, Houston, TX, September, 1993.
- "Corrosion and Corrosion Fatigue of Aircraft Aluminum Alloys", **Robert P. Wei**, FAA/NASA Corrosion Working Group Meeting, Lehigh University, Bethlehem, PA, November 2, 1993.
- "Corrosion and Corrosion Fatigue of Aircraft Aluminum Alloys", R. P. Wei, Materials Degradation Panel of USAF Scientific Advisory Board, Arlington, VA, January 19, 1994.
- "Corrosion and Corrosion Fatigue of Airframe Materials", R. P. Wei, FAA Meeting, Salt Lake City, UT, March 24, 1994.
- "Corrosion and Corrosion Fatigue of Airframe Aluminum Alloys", G. S. Chen, M. Gao, D. G. Harlow and R. P. Wei, FAA/NASA International Symposium on Advanced Structural

Integrity Methods for Airframe Durability and Damage Tolerance, Hampton, VA, May 4-6, 1994.

"Corrosion and Fatigue of Aluminum Alloys: Chemistry, Micromechanics and Reliability", **Robert P. Wei**, Second Air Force Aging Aircraft Conference, Oklahoma City, OK, 17-19 May, 1994.

"Overview of Lehigh Research in Corrosion/Fatigue", R. P. Wei, Air Force Corrosion/Fatigue Research Meeting, Wright Laboratory, WPAFB, OH, June 3, 1994.

"A Probability Model for Pitting Corrosion in Aluminum Alloys", **D. G. Harlow**, G. Chen and Robert P. Wei, Proceedings of U.S. National Congress for Applied Mechanics, Seattle, WA, June 26-July 1, 1994.

"Corrosion and Corrosion Fatigue in Airframe Materials", R. P. Wei, CAA/FAA Workshop on Corrosion Fatigue Interactions, Cranfield University, Cranfield, England, July, 1994.

"Corrosion and Corrosion Fatigue in 2024-T3 and 7075-T6 Aluminum Alloys", **Robert P. Wei**, AFOSR URI meeting on Corrosion, Tribology, Lubrication and Materials Fatigue under Extreme Conditions, University of Illinois, Urbana, IL, August 17-18, 1994.

"Pitting Corrosion and Short Crack Growth", R. P. Wei, FAA/NASA Corrosion Working Group meeting, SRI, Menlo Park, CA, November 2-3, 1994.

"Corrosion and Fatigue of Aluminum Alloys: Chemistry, Micromechanics and Reliability", **R. P. Wei**, Corrosion/Fatigue Program Planning Meeting, U. S. Air Force, Wright Laboratory/Flight Dynamics Directorate, WPAFB, OH, February 8-9, 1995.

"A Mechanistically Based Probability Approach for Life Prediction", **Robert P. Wei** and D. Gary Harlow, International Symposium on Plant Aging and Life Prediction of Corrodible Structures, Sapporo, Japan, May 15-18, 1995.

"Spatial Statistics of Particles and Corrosion Pits in 2024-T3 Aluminum Alloy", **D. G. Harlow**, N. R. Cawley and R. P. Wei, Proceedings of Canadian Congress of Applied Mechanics, Victoria, British Columbia, May 28-June 2, 1995.

"Pitting Corrosion in Aluminum Alloys", FAA/NASA Corrosion Working Group, **Robert P. Wei**, U.S. DOT/Volpe National Transportation Systems Center (Volpe Center), Cambridge, MA, June 15-16, 1995.

"Environmentally Enhanced Crack Growth in Nickel-Based Alloys at Elevated Temperatures", **M. Gao**, S. F. Chen, G. S. Chen and R. P. Wei, ASTM 27th National Symposium on Fatigue and Fracture Mechanics, Williamsburg, VA, June 26-29, 1995.

"Life Prediction: A Case for Multi-Disciplinary Research", **Robert P. Wei**, ASTM 27th National Symposium on Fatigue and Fracture Mechanics, Williamsburg, VA, June 26-29, 1995.

"Pitting Corrosion in Aluminum Alloys: Experimentation and Modelling", **R. P. Wei**, Ming Gao and D. Gary Harlow, Air Force 3rd Aging Aircraft Conference, Dayton, OH, September 26-28, 1995.

"Transition From Pitting Corrosion to Fatigue Crack Growth in a 2024-T3 Aluminum Alloy", **G. S. Chen**, K.-C. Wan, M. Gao and R. P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.

"In Situ Monitoring of Pitting Corrosion in Aluminum Alloys", **Chi-Min Liao**, Ming Gao and Robert P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.

"Mechanical and Environmental Effect on Growth of Short-Fatigue-Cracks in a 2024-T3 Aluminum Alloy", **K.-C. Wan**, G. S. Chen, M. Gao and R. P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.

"Evolution of Pitting Corrosion in a 2024-T3 Aluminum Alloy", Raymond M. Burynski, Jr., Gim-Syang Chen and **Robert P. Wei**, ASME Winter Annual Meeting, Structural Integrity in Aging Aircraft, San Francisco, CA, November 12-17, 1995.

"A Probability Model for the Nucleation and Coalescence of Corrosion Pits in Aluminum Alloys", **D. Gary Harlow** and Robert P. Wei, ASME Winter Annual Meeting, Structural Integrity in Aging Aircraft, San Francisco, CA, November 12-17, 1995.

"Mechanical and Environmental Effects on Growth of Short Fatigue Cracks in a 2024-T3 Aluminum Alloy", **K.-C. Wan**, G. S. Chen, M. Gao and R. P. Wei, ASTM November Meeting, Task Group E08.06.04 on Small Cracks, Norfolk, VA, November 14, 1995.

"Modelling Corrosion and Corrosion Fatigue for Aging Aircraft", **D. Gary Harlow**, Seminar, Dept. of Theoretical and Applied Mechanics, Cornell University, Ithaca, NY, January 31, 1996.

"A Mechanistically Based Probability Approach for Service Life Prediction", **Robert P. Wei**, Seminar at Rutgers University, Piscataway, NJ, February 21, 1996.

"Pitting Corrosion and Fatigue Crack Nucleation", G. S. Chen, C.-M. Liao, M. Gao and R. P. Wei, ASTM Symposium on Effects of the Environment on the Initiation of Crack Growth, Orlando, FL, May 20-21, 1996.

"Pitting Corrosion Study of Aluminum Alloys by an In-Situ Monitoring Method", Chi-Min

- Liao, Jean-Marc Olive, Ming Gao and Robert P. Wei, ASTM Symposium on Effects of the Environment on the Initiation of Crack Growth, Orlando, FL, May 20-21, 1996.
- "A Mechanistically Based Probability Approach for Service Life Prediction", **Robert P. Wei**, ASME Symposium on Materials and Mechanics Issues in Structural Life Prediction, Johns Hopkins University, Baltimore, MD, June 13-14, 1996.
- "Corrosion and Corrosion Fatigue Aspects of Aging Aircraft", Robert P. Wei, Ming Gao and D. Gary Harlow, Proceedings of Air Force 4th Aging Aircraft Conference, United States Air Force Academy, CO, July 9-11, 1996.
- "Probability and Statistics Modeling of Constituent Particles and Corrosion Pits as a Basis for MSD Analysis", N. R. Cawley, D. G. Harlow and R. P. Wei, FAA-NASA Symposium on Continued Airworthiness of Aircraft Structures, Atlanta, GA, August 28-29, 1996.
- "Mechanistically Based Probabilistic Considerations of Creep Crack Growth", **Robert P.** Wei and D. Gary Harlow, FAA/Air Force Workshop on Application of Probabilistic Methods to Gas Turbine Engines, Dayton, OH, 8-9 October 1996.
- "TEM Studies of Particle-Induced Corrosion in 2024-T3 and 7076-T6 Aluminum Alloys", **Robert P. Wei** and Ming Gao, 1997 TMS Annual Meeting, Orlando, FL, February 9-13, 1997.
- "Identification of Constituent Particles in 2024-T3 and 7075-T6 Aluminum Alloys", **Ming Gao**, Robert P. Wei and Jerry Feng, 1997 TMS Annual Meeting, Orlando, FL, February 9-13, 1997.
- "Grain Boundary Niobium-Rich Carbides in Inconel 718", **Ming Gao** and Robert P. Wei, 1997 TMS Annual Meeting, Orlando, FL, February 9-13, 1997.
- "Corrosion Fatigue Science and Engineering", R. P. Wei, Keynote speaker for The Institute of Materials Symposium on Recent Advances in Corrosion Fatigue, 16-17 April, 1997, Sheffield, UK.
- "Effect of Statistical Variability in Material Properties on Springback Predictability", **D. Gary Harlow**, AEROMAT 97, Williamsburg, VA, May 12-16, 1997.
- "Probability Modeling of Fatigue Crack Growth and Pitting Corrosion", **Robert P._Wei**, Chitang Li, D. Gary Harlow and Thomas H. Flournoy, 19th ICAF Symposium, Edinburgh, 16-20 June 1997.
- "Aging of Airframe Materials: From Pitting to Cracking", Robert P. Wei and D. Gary Harlow, First Joint DoD/FAA/NASA Conference on Aging Aircraft, Ogden, Utah, 8-10 July 1997.

- "Corrosion Modeling", Robert P. Wei, Corrosion Modeling Technical Interchange Meeting, Robbins Air Force Base, GA, August 14, 1997.
- "Life Prediction and Fleet Management: A Case for Multidisciplinary Research", **Robert P. Wei**, Keynote presentation for Workshop on Fatigue, Fracture and Failure (F³), Naval Research Laboratory, Washington, DC, 9-10 September 1997.
- "Progress in Understanding Corrosion Fatigue Crack Growth", **Robert P. Wei**, Proceedings of Symposium on High Cycle Fatigue: The Paul Paris Symposium, 1997 TMS Fall Meeting, Indianapolis, IN, September 14-18, 1997.
- "Aging of Airframe Aluminum Alloys: From Pitting to Cracking", **Robert P. Wei**, Workshop on Intelligent NDE Sciences for Aging and Futuristic Aircraft, El Paso, TX, 30 September-2 October 1997.

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- Robert P. Wei, "Corrosion Fatigue: Science and Engineering", in <u>Recent Advances in Corrosion Fatigue</u>, Sheffield, UK 16-17 April 1997 (to be published).
- Robert P. Wei, Chitang Li, D. Gary Harlow and Thomas H. Flournoy, "Probability Modeling of Corrosion Fatigue Crack Growth and Pitting Corrosion", Proceedings of 19th ICAF Symposium, Edinburgh, UK, 18-29 June 1997, to appear.
- Robert P. Wei and D. Gary Harlow, "Aging of Airframe Materials: From Pitting to Cracking", Proceedings of First Joint DoD/FAA/NASA Conference on Aging Aircraft, Ogden, Utah, July 1997, to appear.

- Robert P. Wei, "Aging of Airframe Aluminum Alloys: From Pitting to Cracking" (Extended Abstract), Proceedings of Workshop on Intelligent NDE Sciences for Aging and Futuristic Aircraft, FAST Center for Structural Integrity of Aerospace Systems, The University of Texas at El Paso, El Paso, TX, September 30-October 2, 1997, ISBN: 87404-279-8, pp. 113-122.
- Chitang Li, D. Gary Harlow and Robert P. Wei, "Probability Modeling of Corrosion Fatigue Crack Growth under Spectrum Loading", submitted to AIAA.
- D.G. Harlow and R. P. Wei, "Probabilistic Aspects of Aging Airframe Materials: Damage versus Detection", Proceedings of the Third Pacific Rim International Conference on Advanced Materials and Processes (PRICM 3), July 12-16, 1998, Honolulu, Hawaii.
- K.-C. Wan, G.S. Chen, M. Gao and R.P. Wei, "Interactions between Mechanical and Environmental Variables for Short Fatigue Cracks in a 2024-T3 Aluminum Alloy in 0.5M NaCl Solutions", in preparation.

4.0 Personnel and Degrees Granted

Faculty and Staff:

- Wei, R. P., Professor, Mechanical Engineering & Mechanics. Dr. Wei served as Principal Investigator for the program and had overall responsibility for program coordination and technical direction.
- Harlow, D. G., Professor, Mechanical Engineering & Mechanics. Dr. Harlow had responsibility for probability modeling.
- Gao, M., Principal Research Scientist, Zettlemoyer Center for Surface Studies. Dr. Gao addressed the microstructural and chemical aspects of corrosion and corrosion fatigue.

Postdocs, Research Scientists and Visiting Scientists:

- Chen, Gim-Syang (non-U.S. citizen), Ph.D., Research Scientist, Zettlemoyer Center for Surface Studies, January, 1992-February 1996. Dr. Chen contributed to the microstructural and chemical aspects of pitting corrosion and crack nucleation.
- Chen, Shuchun (non-U.S. citizen), Ph.D., Postdoctoral Research Associate, Zettlemoyer Center for Surface Studies, January 1994-March 1995. Dr. Chen contributed to the microstructural aspects of the program.
- Olive, Jean-Marc, (non-U.S. citizen), Ph.D., Visiting Scientist (University of Bordeaux, France), January, 1995 December, 1995. Dr. Olive participated in the experimental and modeling aspects of particle-induced pitting corrosion.

Graduate Students and Degrees (including those supported by FAA):

Degrees Granted:

- **Burynski**, Raymond M., Jr. (U.S. citizen), M.S. in Applied Mechanics, January 1994. Thesis: "Corrosion Response of a 2024-T3 Alloy in 0.5M NaCl Solution".
- Cawley, Nancy R. (U.S. citizen), Ph.D. in Applied Mathematics, January 1996. Dissertation: "Models for the Spatial Statistics of Constituent Particles and Corrosion Pits".
- Li, Chitang (non-U.S. citizen), Ph.D. in Applied Mechanics, June 1997. Dissertation: "Probabilistic Modeling for Corrosion Fatigue Crack Growth".
- **Liao**, Chi-Min (non-U.S. citizen), Ph.D. in Materials Science & Engineering, January 1998 (supported by China Steel Corp., Taiwan, 7/94-7/97). Dissertation: "Particle-Induced Pitting Corrosion of Aluminum Alloys".
- Wan, Kuang-Chung (non-U.S. citizen), Ph.D. in Mechanical Engineering & Mechanics, January 1996. Dissertation: "Mechanical and Chemical Aspects of Corrosion Fatigue of a 2024-T3 Aluminum Alloy in the Short Crack Regime".

Continuing Students:

- **Dolley**, Evan J. (U.S. citizen), Ph.D. in Applied Mechanics, expected June 1999. Research area: Short crack growth in 7000 series of aluminum alloys.
- Lee, Baehko (non-U.S. citizen), M.S. in Applied Mechanics, expected June 1998. Research area: Effect of precorrosion on fatigue life.
- **Oshkai**, Svetlana P. (non-U.S. citizen), M.S. in Computational & Applied Mechanics, expected Jan. 1999. Research area: Analysis codes for pitting and corrosion fatigue.

Undergraduate Summer Interns:

DeMoyer, Julie, Summer 1996, U.S. citizen. **Zoleta**, Jeffrey, Summer 1996, U.S. citizen.

Table 1: Chemical composition of aluminum alloys (in wt%)

| Alloy | <u>Cu</u> | Mg | <u>Si</u> | <u>Ti</u> | <u>Cr</u> | <u>Fe</u> | Mn | <u>Zn</u> | <u>Al</u> |
|---------|-----------|------|-----------|-----------|-----------|-----------|------|-----------|-----------|
| 2024-T3 | 4.24 | 1.26 | 0.06 | 0.31 | <0.01 | 0.15 | 0.65 | 0.08 | Balance |
| 7075-T6 | 1.76 | 2.55 | 0.10 | 0.04 | 0.19 | 0.25 | 0.09 | 5.81 | Balance |

Table 2: Corrosion potential of intermetallic compounds and aluminum alloys^{5,6,7,8}

| Stoichiometry or Alloy | Corrosion Potential (mV SCE) | Environment | Aeration | Ref. Footnote |
|------------------------|------------------------------|------------------------------|-------------|------------------|
| Al ₂ Cu | -700 | 0.5M NaCl | Open to air | 5 |
| Al_2Cu | -640 | 53 g/L NaCl + 3 g/L H_2O_2 | Open to air | 5 |
| Al_2Cu | -621 | 3% NaCl | Not stated | 5 |
| Al_2Cu | -680 | 0.2M NaCl | Not stated | 5 |
| Al ₂ CuMg | -890 | 1.0M NaCl | Open to air | 5 |
| Al ₂ CuMg | -910 | 53 g/L NaCl + 3 g/L H_2O_2 | Open to air | 5 |
| Al ₃ Fe | -470 | 53 g/L NaCl + 3 g/L H_2O_2 | Open to air | 5 |
| Al ₃ Fe | -580 to -390 | 3% NaCl | Not stated | 5 |
| Al ₃ Fe | -485 | 0.5M NaCl | Open to air | 8 |
| 2024-T3 | -600 | ASTM G69 | Not stated | 6,7 |
| 2024-T3 | -605 | 0.5M NaCl | Open to air | 21 |
| 7075-T6 | -740 | ASTM G69 | Not stated | 6,7 |
| 7075-T6 | -750 | 0.5M NaCl | Open to air | 8 |
| Al (99.9%) | -730 | 0.5M NaCl | Open to air | 8 |
| Al (99.999%) | -750 | ASTM G69 | Not stated | 6 |
| Cu (99.9%) | -200 | 0.5M NaCl | Open to air | 6,7 |
| Cu (99.999%) | 0 | ASTM G69 | Not stated | 6 |

⁵ R.G. Buchheit, *J. Electrochem. Soc.*, <u>142</u> (11), pp. 3994-96 (1995).

⁶ T.D. Butleigh, R.C. Rennick and F.S. Bovard, *Corrosion*, <u>49</u> (8), pp. 683-5 (1993).

⁷ ASM Specialty Handbook: Aluminum and Aluminum Alloys, ASM International, Materials Park, OH, p. 581 (1994).

⁸ Chi-Min Liao, Ph.D. Dissertation, Lehigh University, Bethlehem, PA (1997).

Pitting Corrosion

Crack Nucleation and Growth SIZE Threshold for Crack Growth £2 ★ Transition to DEFECT £3 Crack Growth f4 Crack Growth Dominated \mathbf{a}_{tr} $a_{\rm th}$ Corrosion **Dominated** $t_{\rm tr}$ TIME (N/f)

Figure 1: Schematic representation of pitting corrosion and corrosion fatigue.

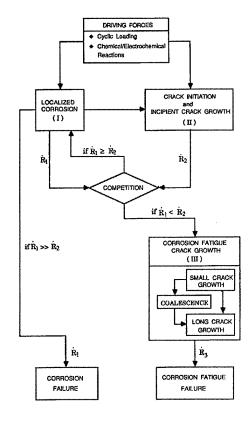


Figure 2: Flow diagram showing the overall processes for corrosion and fatigue damage.

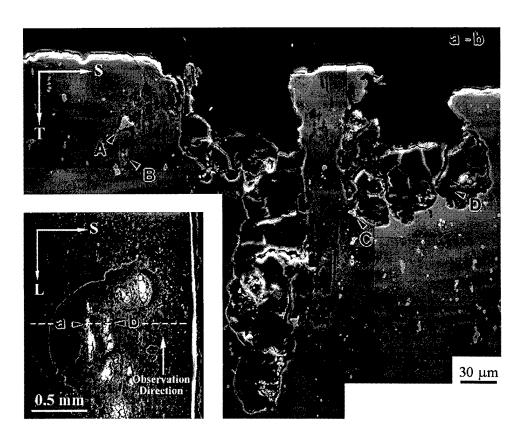


Figure 3: SEM micrograph of the cross-section of severe corrosion pits in a 2024-T3 alloy (TS) surface along with an inset, showing the corresponding surface appearance of the pits.

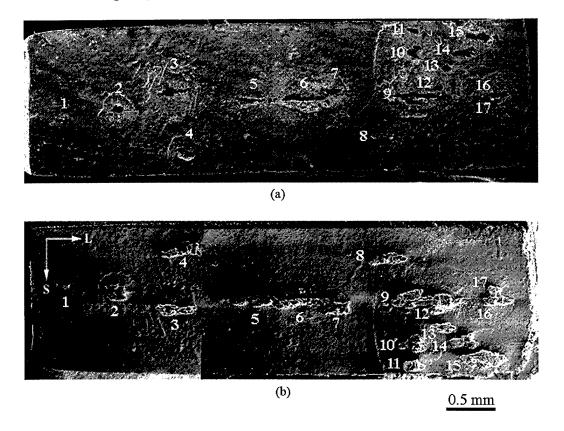


Figure 4: (a) The LS surface of a 2024-T3 aluminum alloy specimen after 500 h in 0.5M NaCl solution, and (b) the corresponding 3-D replicas.

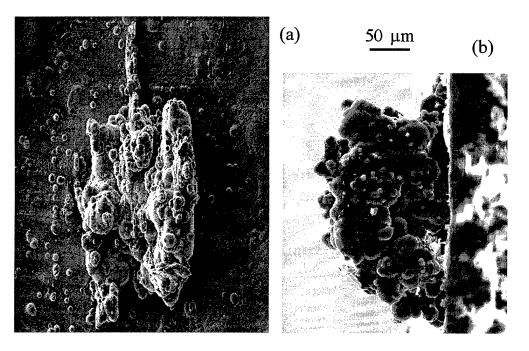


Figure 5: Replica corresponding to pit 2 in Fig. 4: (a) plan (bottom) view, and (b) elevation (side) view; relative to the original pit.

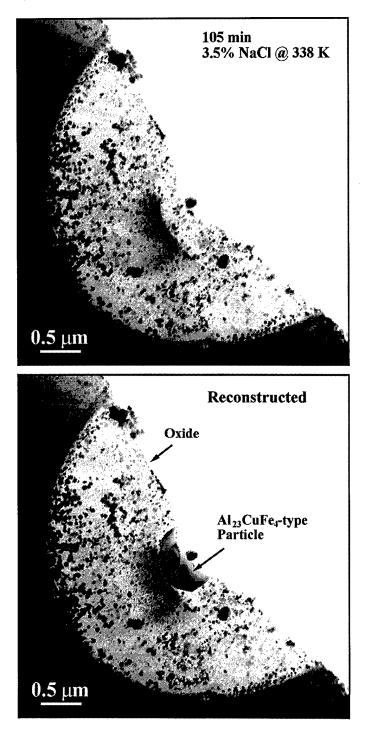


Figure 6: TEM micrograph of 7075-T651 aluminum alloy showing oxide left behind by particle-induced corrosion: (a) residual oxide, and (b) reconstructed image showing position of original particle.

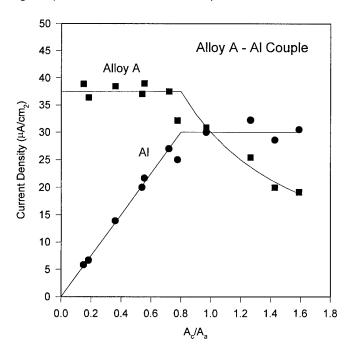


Figure 7: Comparison of *anodic* and *cathodic* current densities as a function of cathode-to-anode surface area ratio for an Al (*anode*) – Alloy A (*cathode*) couple in 0.5M NaCl solution at room temperature.

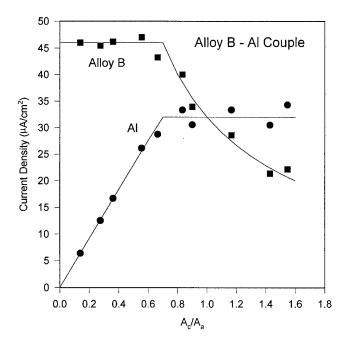


Figure 8: Comparison of *anodic* and *cathodic* current densities as a function of cathode-to-anode surface area ratio for an Al (*anode*) -- Alloy B-Al couple in neutral 0.5M NaCl solution.

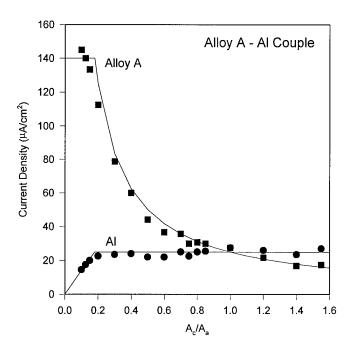


Figure 9: Comparison of *anodic* and *cathodic* current densities as a function of cathode-to-anode surface area ratio for an-Al (anode) – Alloy A (cathode) couple in 0.5M NaCl + 0.07M AlCl₃ solution (pH \approx 3.5).

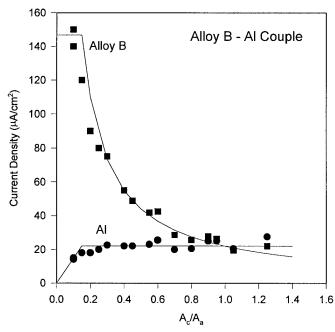
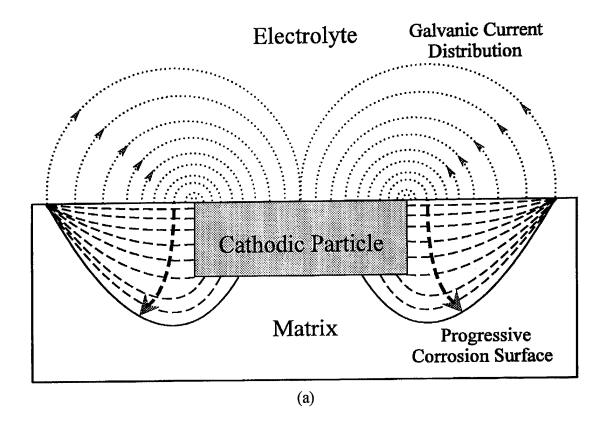


Figure 10: Comparison of *anodic* and *cathodic* current densities as a function of cathode-to-anode surface area ratio for an-Al (*anode*) – Alloy B (*cathode*) couple in 0.5M NaCl + 0.07M AlCl₃ solution (pH ≈ 3.5).



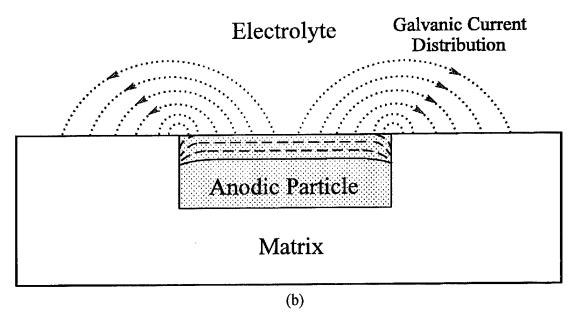
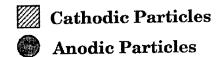


Figure 11: Conceptual models of particle-matrix interactions (local corrosion) for (a) a cathodic and (b) an anodic particle.



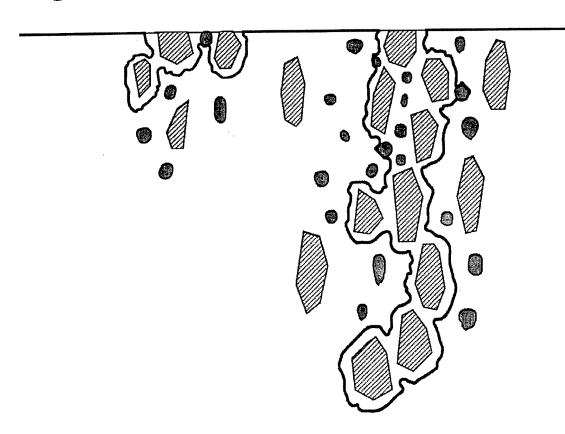


Figure 12: Schematic diagram of a conceptual model for pitting in the transverse orientation involving matrix dissolution around clusters of cathodic constituent particles.

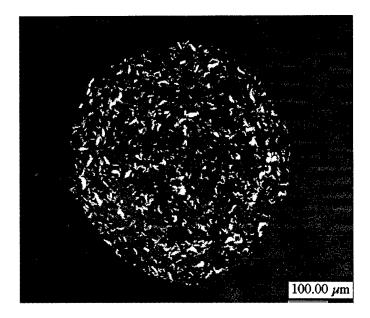


Figure 13: SEM micrograph showing the distribution of copper particles in an artificial cluster.

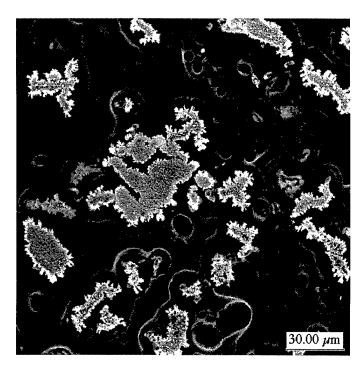


Figure 14: SEM micrograph showing matrix dissolution surrounding copper particles in an artificial cluster.

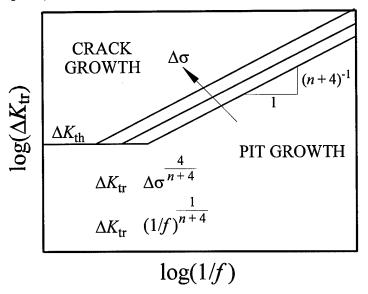


Figure 15: Schematic of a proposed corrosion/fatigue map showing the relationship between stress intensity factor range and frequency with the applied cyclic stress range as a parameter.

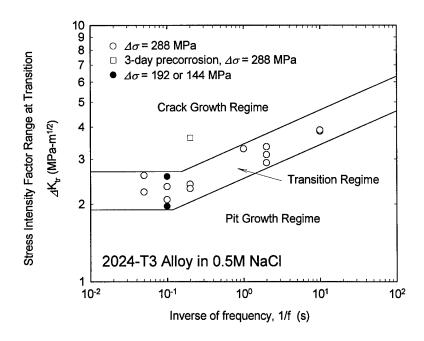


Figure 16: The relationship between the stress intensity factor range of equivalent cracks at fatigue crack nucleation and the frequency of applied cyclic stress.

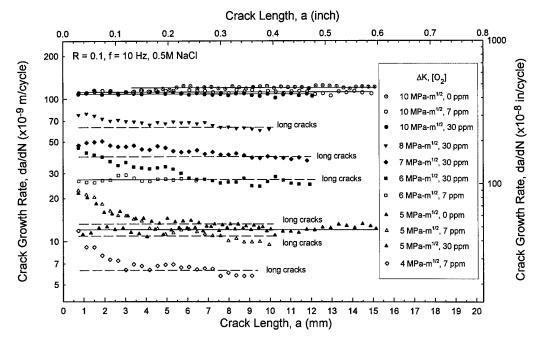


Figure 17: Fatigue crack growth rates at various ΔK levels in 0.5M NaCl at three oxygen levels for 2024-T3 aluminum alloy.

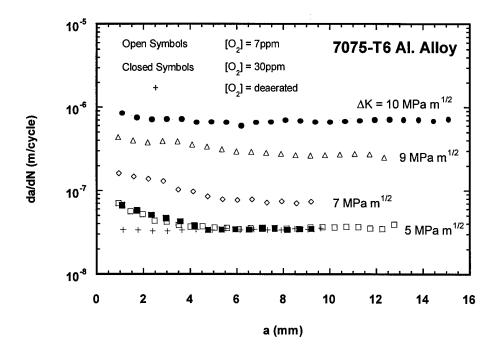


Figure 18: Fatigue crack growth rates at various ΔK levels in 0.5M NaCl at thre oxygen levels for 7075-T6 aluminum alloy.

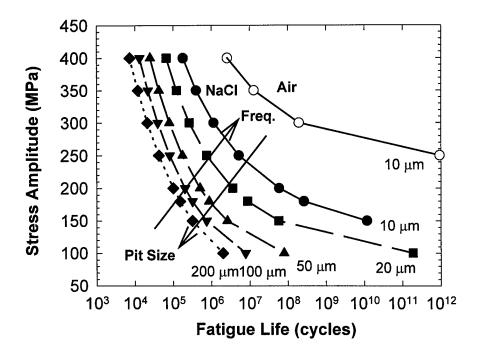


Figure 19: The influence of stress and initial pit (crack) size on fatigue life.

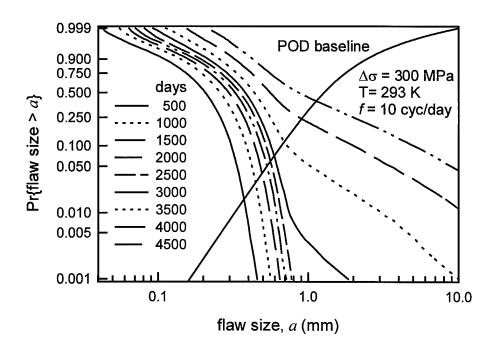


Figure 20: Probability of flaw size for a given time at 293 K and 10 cyc/day.

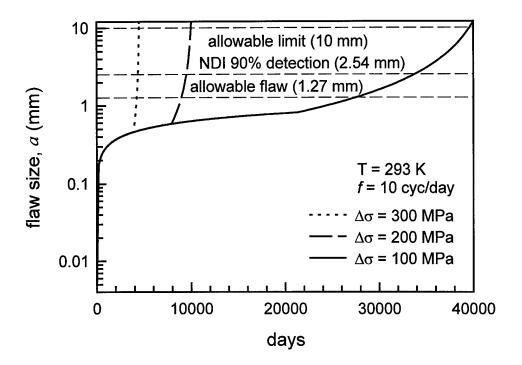


Figure 21: Average flaw size as a function of time at 293 K and 10 cyc/day.

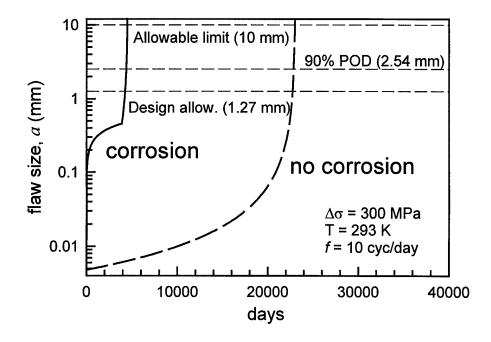


Figure 22: Average flaw size modeled by pitting corrosion with CFCG and CFCG only as a function of time for 300 *MPa*, 293 *K* and 10 *cyc/day*.

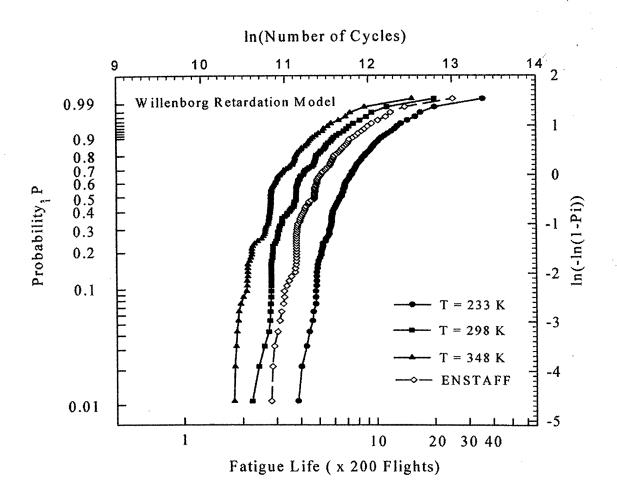


Figure 23: CDF for fatigue lives showing the influences of temperature and temperature spectrum (ENSTAFF) under FALSTAFF spectrum loading.